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Stepwise Transformation of the Molecular Building Blocks in a Porphyrin-Encapsulating Metal–Organic Material

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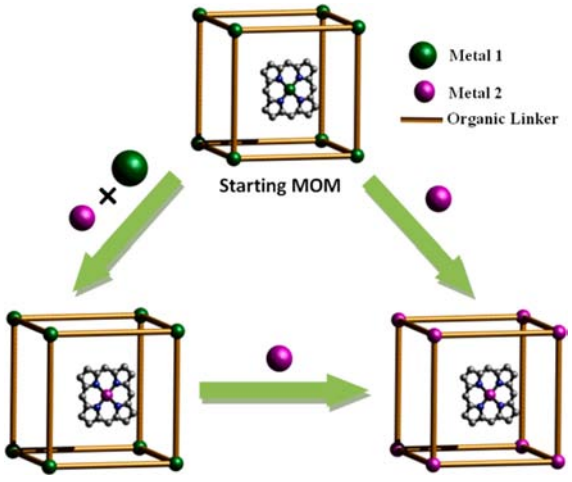
Supporting Information

ABSTRACT: When immersed in solutions containing Cu(II) cations, the microporous metal–organic material **P11** ($[Cd_4(BPT)_4]\cdot[Cd(C_{44}H_{36}N_8)(S)]\cdot[S]$, BPT = biphenyl-3,4′,5-tricarboxylate) undergoes a transformation of its $[Cd_2(COO)_6]^{2-}$ molecular building blocks (MBBs) into novel tetranuclear $[Cu_4X_2(COO)_6(S)_2]$ MBBs to form **P11-Cu**. The transformation occurs in single-crystal to single-crystal fashion, and its stepwise mechanism was studied by varying the Cd^{2+}/Cu^{2+} ratio of the solution in which crystals of **P11** were immersed. **P11-16/1** (Cd in framework retained, Cd in encapsulated porphyrins exchanged) and other intermediate phases were thereby isolated and structurally characterized. **P11-16/1** and **P11-Cu** retain the microporosity of **P11**, and the relatively larger MBBs in **P11-Cu** permit a 20% unit cell expansion and afford a higher surface area and a larger pore size.

Porous metal–organic materials (MOMs) that incorporate reactive species (RS) such as metalloporphyrins,[1] metallosalens,[2] and polyoxometalates[3] are of topical interest because they can combine the physicochemical properties of the RS[4] with permanent porosity of the framework.[5] Such MOMs can thereby enable new approaches to gas storage,[6] separations,[7] luminescence, and catalysis,[8] including enzymatic catalysis.[8b] MOMs that incorporate RS can be divided into two subgroups: those with RS as an integral part of nodes/linkers (**RSMOMs**)[9] and those that encapsulate or host RS in cages (**RS@MOMs**).[10] Encapsulation may be achieved directly through synthesis[11] or via postsynthetic modification (PSM).[12] Metalloporphyrins are attractive RS because of their value as catalysts[13] and dyes,[14] and we recently reported the generation of porphyrin-encapsulating MOMs (**porph@MOMs**)[15] that exhibit PSM through metal ion exchange[16] or metal salt incorporation.[17] The availability of such **porph@MOMs** offers the opportunity to study their PSM systematically and evaluate its impact on their properties such as gas sorption, luminescence, and catalysis. In addition, PSM can afford new compounds that cannot be directly synthesized.

PSM involving metal exchange in molecular building blocks (MBBs) is now widely studied and tends to focus upon Cd- and Zn-containing MOMs[18] because of the relative lability of complexes of d^{10} ions (Cd^{2+}, Zn^{2+}, and Hg^{2+}).[19] The metal exchange process is typically monitored using atomic absorption spectroscopy (AAS) and powder X-ray diffraction (PXRD), and examples where PSM has been followed using single-crystal X-ray diffraction (SCXRD) are rare.[16,20] Since Cd^{2+} in cadmium porphyrins can be irreversibly exchanged with Cu^{2+},[21] the possibility of selective control of PSM in **porph@MOMs** exists if the MOM and the encapsulated RS exhibit different rates of exchange. In this work, we addressed such a situation through the study of crystals of **porph@MOM-11** (**P11**), a Cd-sustained MOM that encapsulates CdTMPyP cations [H_2TMPyP = *meso*-tetra(*N*-methyl-4-pyridyl)porphine tetratosylate]. **P11** was immersed in methanol solutions of Cd^{2+} and/or Cu^{2+} to study how the Cd^{2+}/Cu^{2+} mole ratio impacts PSM. Scheme 1 shows how **porph@MOMs** might generally undergo complete or partial metal exchange through control of the ratio of two metal ions.

Scheme 1. Metal Ion PSM in porph@MOMs: (i) Partial PSM with Metal 2 in the Presence of Both Metal 1 and 2 (Bottom Left); (ii) Complete Exchange with Metal 2 (Bottom Right)



The reaction of biphenyl-3,4′,5-tricarboxylic acid (H_3BPT)[22] and $Cd(NO_3)_2$ with H_2TMPyP afforded **P11**, a microporous MOM in which encapsulated cationic porphyrins occupy alternating channels.[17] **P11** is based upon a 3,6-connected **rtl** net built from two 6-connected $[Cd_2(COO)_6]^{2-}$ MBBs [Figure 1a and Figure S1 in the Supporting Information (SI)]. As illustrated in Figure S1, one MBB is a distorted paddlewheel formed by seven-coordinate Cd^{2+} and the other is a more regular

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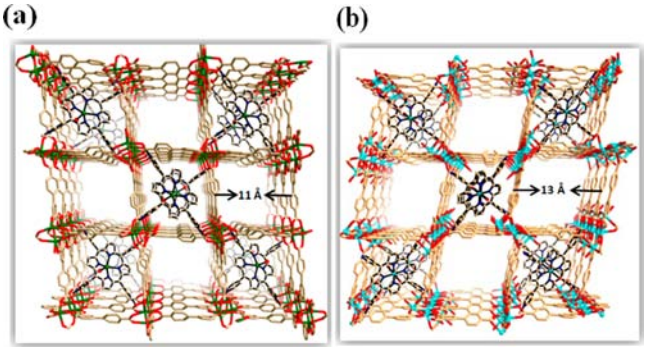

Figure 1. Crystal structures of (a) **P11** and (b) **P11-Cu** viewed down the crystallographic *a* axis.

paddlewheel formed by six-coordinate Cd^{2+}. CdTMPyP cations are alternately arranged in 1D channels, and the remaining channels are occupied by solvent molecules (Figure 1a). The anticipated lability of Cd^{2+} and the readily accessible pores of **P11** [permanent porosity, Brunauer–Emmett–Teller (BET) surface area = 997 m^2/g] offer the potential for PSM through metal ion exchange. Indeed, when crystals of **P11** were immersed in 0.05 M $Cu(NO_3)_2$ in MeOH for 10 days with refreshment of the solution three times, they were transformed into a new crystalline MOM, **P11-Cu** (Figure 1b), which suggested a single-crystal to single-crystal (SC-to-SC) process. Moreover, **P11-Cu** cannot be directly synthesized under the conditions used for PSM, making its formation by a dissolution and recrystallization process unlikely.[18h] AAS revealed complete exchange of the Cd^{2+} cations in **P11** with Cu^{2+}. SCXRD of **P11-Cu**, $[Cu_8(X)_4(BPT)_4(S)_8]\cdot[NO_3]_4\cdot[Cu(C_{44}H_{36}N_8)S]\cdot[S]$ (S = MeOH, H_2O; X = CH_3O^-, OH^-), revealed a larger unit cell than in **P11**, with an associated unit cell volume expansion from 3779.3(2) to 4133.0(5) $Å^3$ (Table S4 in the SI). This can be attributed to the transformation of the dimetallic $[Cd_2(COO)_6]^{2-}$ MBBs of **P11** into larger 6-connected tetrametallic $[Cu_4X_2(COO)_6(S)_2]$ MBBs. To our knowledge, this type of transformation is unprecedented in MOM chemistry.

The use of synchrotron radiation enabled a structural study of the transformation of **P11** to **P11-Cu**. Comparison of the novel $[Cu_4X_2(COO)_6(S)_2]$ MBB in **P11-Cu** with the starting MBB in **P11** (Figure 2) revealed that there are two crystallographically

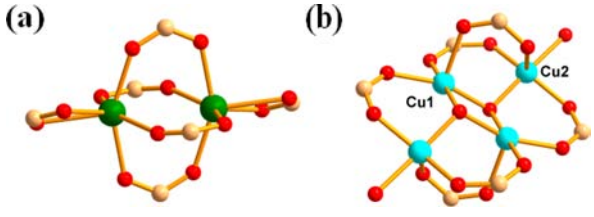

Figure 2. (a) Dinuclear Cd^{2+} MBB in **P11**. (b) Novel tetranuclear Cu^{2+} MBB in **P11-Cu**.

independent five-coordinate Cu^{2+} cations. The coordination environment of Cu1 can be approximately described as trigonal-bipyramidal and consists of two μ_3-X and three monodentate O atoms of bridging carboxylate moieties. The Cu1–O bond distances lie in the range 1.928(4)–2.210(4) Å, and the O–Cu1–O bond angles range from 84.8(2) to 177.9(2)°. Cu2 exhibits a geometry similar to that of Cu1: it is bonded to one μ_3-X, three monodentate O atoms of bridging carboxylate moieties, and one solvent O atom; the Cu2–O bond distances range from 1.929(4) to 2.150(5) Å, and the O–Cu2–O bond angles range from 82.5(2) to 174.2(2)°. The μ_3-X moieties of the MBB are crystallographically disordered OH^- or CH_3O^- anions[23] with Cu–O distances of 1.933(5)–2.007(4) Å. The overall geometry of the MBB in **P11-Cu** can be described as pseudo-octahedral, and therefore, the MBB serves the same structure-directing/building role as the starting 6-connected MBB in **P11**. However, the distances between the C atoms of opposite carboxylate moieties range from 6.05 to 7.63 Å in **P11-Cu**, versus the corresponding values of 5.45–8.61 Å in **P11**. **P11-Cu** therefore exhibits larger 1D channels than **P11**, with the pore size (i.e., the distance between opposite pore walls minus the van der Waals radii) expanding from ca. 11.0 to ca. 13.0 Å. In addition, the encapsulated CdTMPyP cations were converted into CuTMPyP cations, as verified by the solution-state UV–vis spectrum of the dissolved crystals (Figure S2). Attempts to prepare **P11-Cu** directly by reaction of Cu salts with H_3BPT were unsuccessful.

The transformation of **P11** to **P11-Cu** is not readily reversible, as AAS analysis after **P11-Cu** had been immersed in 0.05 M $Cd(NO_3)_2$ in MeOH for 10 days revealed that almost no Cu^{2+} was exchanged with Cd^{2+} (Table S5). This observation contrasts with that of Kim and co-workers.[20] The bond distances and geometries in **P11** and **P11-Cu** were consistent with the expected values, as analysis of the Cambridge Structural Database (ConQuest version 1.14, Aug 2012 update[24]) revealed that Cd^{2+} favors six- or seven-coordinate environments with Cd–O bond distances of ca. 2.28 Å whereas Cu^{2+} tends to favor five- or six-coordinate environments with Cu–O bond distances of ca. 1.96 Å.

We further studied the metal exchange process by treating **P11** with $Cd(NO_3)_2/Cu(NO_3)_2$ in MeOH solutions in which the total metal ion concentration was fixed at 0.05 M. After immersion in a variety of such solutions for 10 days (with refreshment of the solution three times), the resulting crystals were harvested and characterized. When the Cd^{2+}/Cu^{2+} ratio was 2:1, crystals of **P11-2/1** with a unit cell similar to that of **P11-Cu** were obtained (Table S4). AAS and UV–vis spectroscopy confirmed that Cd^{2+} was fully exchanged with Cu^{2+} in both the framework and the porphyrin moiety (Table S5 and Figure S2). However, when Cd^{2+}/Cu^{2+} ratios of 4:1 and 8:1 were used, the resulting phases (**P11-4/1** and **P11-8/1**, respectively) were observed to exhibit unit cell parameters close to those of **P11**. SCXRD indicated that the Cd^{2+} paddlewheels were only partially exchanged with Cu^{2+}. However, UV–vis spectroscopy indicated that the Cd^{2+} cations in CdTMPyP were fully exchanged with Cu^{2+} cations. AAS revealed that 86.6 and 77.5% of the Cd^{2+} cations in the MBBs of **P11-4/1** and **P11-8/1**, respectively, were exchanged with Cu^{2+}. To ascertain whether or not **P11-4/1** and **P11-8/1** could be reversibly exchanged, crystals were immersed in 0.05 M $Cd(NO_3)_2$ in MeOH for 10 days. Analysis of the resulting crystals by AAS showed that the amount of exchanged Cu^{2+} cations in the MBBs had decreased to 55 and 46%, respectively. UV–vis spectroscopy indicated that the Cu^{2+} cations of the CuTMPyP moieties were not exchanged over the 10 day period (Figure S2). These observations imply that metal exchange can be reversible in partially exchanged MBBs but is irreversible in CuTMPyP moieties. When the Cd^{2+}/Cu^{2+} ratio was increased to 16/1 to afford crystals of **P11-16/1**, the unit cell was measured to be that of **P11** and structure refinement showed no evidence of exchange of Cd^{2+} with Cu^{2+} in the MBBs. However, the Cd^{2+} ions in the CdTMPyP moieties were completely exchanged, as verified by SCXRD and UV–vis spectroscopy (Figure S2). AAS suggested that <4% of the Cd^{2+}

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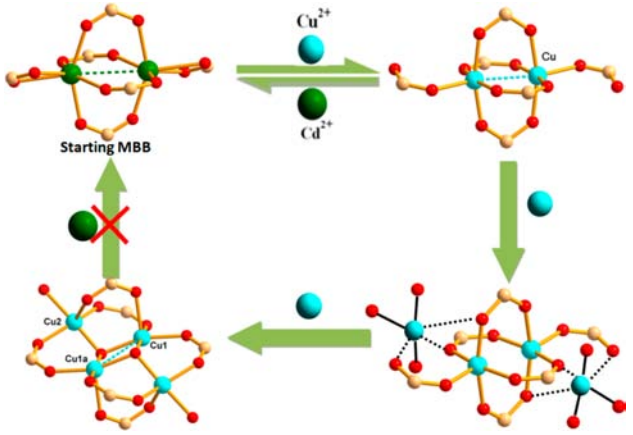
was exchanged with Cu^{2+} in the Cd^{2+} MBBs. Further immersion of crystals of **P11-16/1** into 0.05 M $Cd(NO_3)_2$ for 10 days did not lead to exchange of the Cu^{2+} cations in CuTMPyP, as verified by UV−vis spectroscopy and AAS. In addition, attempts to prepare **P11-16/1** directly by reactions of $Cd(NO_3)_2$ with H_3BPT and CuTMPyP were unsuccessful.

To elucidate further the formation of $[Cu_4X_2(COO)_6(S)_2]$ MBBs in **P11-Cu**, **P11-8/1** was immersed in 0.05 M $Cu(NO_3)_2$ for 10 days. The harvested crystals exhibited the unit cell parameters a = 10.715(5) Å, b = 18.735(5) Å, c = 21.170(5) Å, α = 89.453(5)°, β = 88.294(5)°, γ = 85.071(5)°, and V = 4232(2) Å^3, suggesting that the transformation to **P11-Cu** had occurred. As revealed in Scheme 2, Cd^{2+} paddlewheels were partially

Scheme 2. Possible Pathway to $[Cu_4X_2(COO)_6(S)_2]$ MBBs Starting from $[Cd_2(COO)_6]^{2-}$ MBBs As Determined by Metal Ion Exchange and SCXRD



exchanged to form dinuclear Cu^{2+} paddlewheels in which the metal···metal distance had decreased from ca. 3.33 Å in **P11** to ca. 3.25 Å in **P11-8/1**. These Cu^{2+} paddlewheels contain monodentate carboxylate ligands in the axial sites. When **P11-8/1** was treated with a more concentrated solution of Cu^{2+}, the Cu^{2+} paddlewheels can possibly bind two solvated Cu^{2+} cations in such a manner that they are chelated by three carboxylate O atoms to form a Cu_4 intermediate (Scheme 2, bottom right). This Cu_4 intermediate is consistent with our recent observation that salt addition of Ba^{2+}cations to Cd paddlewheels can occur via coordination through three carboxylate O atoms in **porph(Cl$^-$)@MOM-11(Ba^{2+})** (Figure S3).[17] The Cu_4 intermediate subsequently undergoes a rearrangement to form the tetrametallic $[Cu_4X_2(COO)_6(S)_2]$ MBB that sustains **P11-Cu**.

Thermogravimetric analysis (TGA) revealed that **P11-Cu** and **P11-16/1** exhibit approximately the same weight loss (ca. 13.5%) below 110 °C and thereafter are stable to 250 and 300 °C, respectively (Figure S4). Supercritical CO_2[25] was used to activate the samples for gas sorption measurements. The porosity of the PSM product **P11-16/1** (BET surface area = 1009 m^2/g, Langmuir surface area = 1127 m^2/g) is comparable to that of **P11** (BET surface area = 997 m^2/g, Langmuir surface area = 1096 m^2/g), and **P11-16/1** has a N_2 uptake of 265 cm^3 (STP)/g at 77 K and P/P_0 = 0.95 (Figure 3a). The slightly higher surface area of **P11-16/1** can be ascribed to its slightly lower density (1.024 g/cm^3 vs 1.050 g/cm^3 for **P11**). At 77 K and P/P_0 = 0.95, **P11-Cu** was found to sorb a relatively large amount of N_2 [345 cm^3 (STP)/g]. The calculated BET and Langmuir surface areas were 1251 and 1406 m^2/g, respectively. The pore size distribution

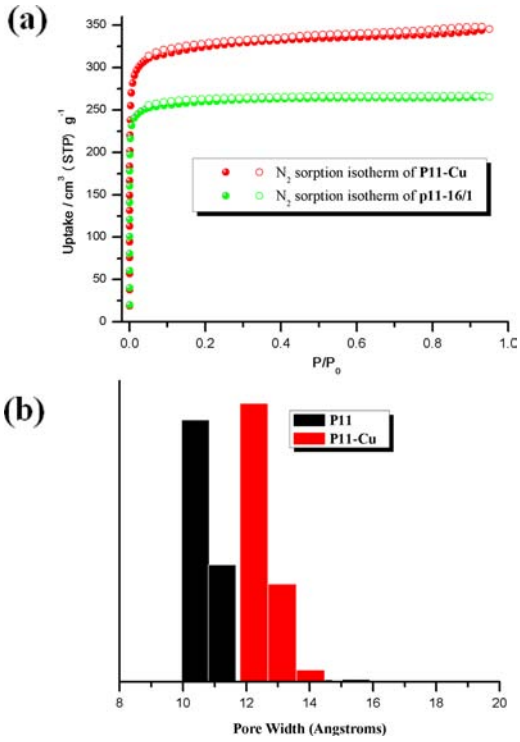


Figure 3. (a) N_2 sorption isotherms at 77 K for **P11-16/1** and **P11-Cu**. (b) Pore size distributions for **P11** and **P11-Cu**.

determined using N_2 revealed that **P11-Cu** has micropores with sizes of ca. ∼13 Å (vs 11 Å in **P11**; Figure 3b), consistent with the crystal structure. CO_2 sorption was also studied, and **P11-Cu** was found to exhibit smaller uptake than **P11** (49 vs 59 cm^3/g, respectively) at 298 K and 1 atm. This observation suggests that the isosteric heat (Q_{st}) of CO_2 adsorption is lower for **P11-Cu** than for **P11**. Indeed, calculations based on CO_2 isotherms collected at 273 and 298 K (Figures S5 and S6) revealed that the initial Q_{st} for **P11-Cu** is 29.8 kJ/mol, versus 30.3 kJ/mol for **P11** (Figure S7). A decrease in Q_{st} for CO_2 as the pore size increases has been seen in other MOMs.[26,27] The Q_{st} for CO_2 in turn impacts the selectivity for CO_2. IAST[28] calculations based on the experimental CO_2 and CH_4 isotherms at 298 K are presented in Figure S8. **P11-Cu** has a lower selectivity for CO_2 versus CH_4 than the parent **P11** over the entire studied pressure range. The initial selectivity of **P11-Cu** was calculated to be 5.0 versus 7.1 for **P11**. This observation is also consistent with other studies on the effect of pore size on gas sorption.[27]

In conclusion, the Cd^{2+}-based **porph@MOM P11** is a versatile platform that can undergo metal ion exchange with Cu^{2+} in an SC-to-SC fashion. The use of mixed metal salt solutions (Cu^{2+}/Cd^{2+}) with varying ratios of metal salts enabled a systematic study of the metal exchange process in **P11**, which showed that at one extreme only the Cd^{2+} porphyrin moieties undergo metal ion exchange, whereas at the other extreme the ions in both the framework and the porphyrin moieties are fully exchanged. In addition, for the first time we have observed a phenomenon in which the MBBs of the parent compound **P11** are transformed from a dimetallic MBB to a larger, previously uncommon tetrametallic MBB, thereby increasing unit cell size, pore size, and surface area.

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■ ASSOCIATED CONTENT

Supporting Information

Crystal data (CIF); UV−vis, TGA, and PXRD data; supplemental structure pictures; and CO_2 adsorption isotherms, Q_{st} plots, and selectivity plots. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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